

THE DETONATION OF
SOLID EXPLOSIVES

BY

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SOLID EXPLOSIVES

by

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INTRODUCTION

The purpose of this paper is to examine and correlate the various physical and chemical relations proposed to explain the phenomena of detonation, in particular, the detonation of solid explosives. In order to assure a reasonably comprehensive treatise, it is desirable at the outset to devote some attention to the correction of certain widespread misconceptions regarding explosives and their behavior. Two distinct types of explosion processes, deflagration and detonation, are evidenced by materials referred to as explosives. It has been common practice, especially in the early literature on the subject, to distinguish between the two on the basis of chemical composition of the explosive and its intended application. Deflagration is invariably associated with "low" explosives or propellants and the continual employment of certain explosives such as nitrocellulose and black powder for their propulsive effect has led to the erroneous association of chemical compositions with the type of behavior. Similarly the detonation process is associated with primary and "high" explosives and likewise is considered to be the sole type of behavior evidenced by other chemical substances. Unfortunately the above classification is not borne out by facts. On the contrary, experimental results indicate that all explosives are capable of exhibiting both modes of behavior. In view of this it is necessary to establish some criterion other than chemical composition to enable one to distinguish clearly between the two processes.

The deflagration process, in its broadest sense, can be considered a rapid burning in which the essential rate-determining factor is the speed of the chemical reaction. That is, the rate at which the

deflagration proceeds is related directly to the kinetics of the reaction taking place in the burning zone.

The propagation of deflagration is closely associated with transport mechanisms; either the transport of heat or of atoms and free radicals acting as chain-carriers or a combination of the two. As long as mechanisms such as these control the propagation, there is established a limiting velocity beyond which the rate of deflagration cannot pass. Extensive investigations have been carried out in connection with the process of deflagration in a gaseous medium and several excellent treatments are available (1,2).

In the case of detonation, the characteristic feature distinguishing the process is the appearance of a pressure wave propagating at a high velocity. The rate at which detonation proceeds is calculable by means of hydrodynamic and thermodynamic equations without the necessity of reaction-kinetic data. The application of the classical hydrodynamic-thermodynamic theory requires no assumptions regarding chemical mechanisms other than the postulate that the reactions occur at such a rate so as not to be a limiting factor.

This theory, which is reviewed in detail, is based upon expressions for the continuity of mass, momentum and energy across a so-called detonation front and upon the assumption that the stable detonation velocity is the minimum one compatible with the conservation equations. When supplemented by an equation of state and thermal data for the products of reaction, the theory permits the calculation of detonation velocity, temperature and pressure, as well as other parameters of interest.

INITIATION AND PROPAGATION OF DETONATION

The currently accepted hydrodynamic detonation theory, which will be discussed in a later section, unfortunately provides no information concerning the mechanism by which a stable detonation wave arises. It is well established by experience that detonation can be brought about by a wide variety of conditions, including mechanical shock, high temperature, friction, and adiabatic compression of interstitial gas. Only recently, however, have successful attempts been made towards the establishment of what might be considered a generalized theory of initiation. The work of S. J. Jacobs and D. P. MacDougall (3) at the Explosives Research Laboratory of the N.D.R.C. involving the controlled deflagration of readily detonable substances and that of F. P. Bowden and his associates (4) on the isolation of factors responsible for thermal ignition provided a basis upon which such a theory could be proposed. The approach adopted by both G. B. Kistiakowsky (5) and A. R. Ubbelohde (5) is that of a preliminary deflagration evolving discontinuously into a detonation.

Consider a mass of explosive particles in which a small peripheral deflagration has been started. As the deflagration spreads inward, pressure gradients develop due to the restricted flow of the gaseous products through the interstices between the particles. As the interior pressure rises, the speed of the deflagration increases, resulting in a faster decomposition and a further increase in pressure. This constantly increasing deflagration may evolve into a stationary combustion in which the flow of heat and material away from the reaction zone compensates for that produced by the reactions, or the deflagration rate

may continue to increase until all the material is consumed provided the mass of explosive involved is less than the "critical size". The concept of "critical size" for a particular explosive is a function of many variables including shape (volume-area ratio), particle size, crystal form for polymorphic substances, and density. It is probably best defined, although somewhat nebulously, as a limiting criterion, that is, the critical size is that size at which the rate of decomposition undergoes a discontinuity. The discontinuity may result in a partial or complete extinguishing of deflagration, with perhaps a re-initiation at an adjacent spot in the substance or it may be evidenced by the phenomenon of detonation. To see how the non-stationary deflagration might evolve into a detonation we must consider the flow of gases from a center of deflagration in more detail. As each crystal decomposes it acts as a center from which the gas molecules stream outwards, thus forming a pressure wavelet. If a number of these wavelets can integrate to give a streaming velocity corresponding to that accompanying a stable detonation wave for the system, we have conditions identical to those observed in a detonation. The type of flow just postulated has a very close analogy in the field of gaseous combustion. A column of gas acted upon by a piston subject to acceleration is frequently cited as an example of the mechanism of shock wave formation in gases. Further discussion of this mechanism is included in the following section.

Assuming a shock wave has developed it is of interest to consider how its passage through the explosive can initiate the decomposition. The details of the mechanism by which a shock with its discontinuous rise in pressure and non-isentropic temperature effects activate

the explosive molecules is still the subject of considerable speculation.

It has been proposed by Ubbelohde (5) that the most probable mechanism for the propagation of detonation is the collision of high speed atoms, radicals or molecules from behind the wave front with the quiescent layer of molecules just ahead of the front. Particles behind the detonation front are assumed to have an unusually high activation efficiency due to high random velocities at the detonation temperature and a high directed velocity resulting from the hydrodynamic conditions of propagation of a shock wave. Impact of a high speed particle is visualized as disrupting an unreacted molecule before the kinetic energy has had time to be distributed among all the vibrational degrees of freedom. If dissociation occurs after the redistribution of energy, then such a dissociation must be attributed to high temperature in the ordinary sense. Since redistribution requires a small or zero activation energy, whereas dissociation requires an activation energy about equal to the strength of the bond broken, it is probable that redistribution of the kinetic energy will occur before dissociation in most cases.

It has been suggested by Wendlandt (6), Eyring (7) and others that the mechanism of chemical activation depends primarily on the high temperature produced by the shock wave. Although considerable uncertainty exists in regard to reactions at the extreme temperatures and pressures of detonation, it has been shown (8) that the temperature coefficient of the energy-releasing process is much smaller than the usual Arrhenius value. This, plus the fact that it is unlikely that sufficient time exists in the activation process for the vibrational

and rotational quanta to attain the full Maxwell-Boltzman equilibrium, indicates that the temperature effect alone probably does not completely account for the activation.

Still another theory has been proposed suggesting that the pressure in the wave front causes a bending of the molecules placing reactive groups in close proximity to each other, whereupon the decomposition occurs. It is felt that this theory is the least satisfactory of those presented since Bridgeman (9) has shown that high hydrostatic pressure alone has no effect on explosives. This theory is also untenable from the standpoint of chemical mechanism since practically every conceivable first step in the decomposition of organic nitro explosives is endothermic and the pressure activation concept requires an exothermic initial step.

Thus at the present time it appears most reasonable to attribute the propagation of detonation to the energy possessed by the shock wave as a whole rather than to attempt a more detailed and perhaps erroneous description of the phenomenon.

SHOCK WAVES

The theoretical basis for the development of a theory of detonation stems from theory of shock waves proposed by Hugoniot (10) in the nineteenth century. In mathematical language he formulated the difference between shock waves, or compressional waves of finite amplitude, and weak acoustic waves. The former were found to be propagated with velocities which are greater than the acoustic velocity of the medium, the more so the higher the peak pressure in the crest of the wave. The medium itself is moving in the shocks, the wave velocity being slightly less than this mass velocity plus the acoustic velocity. Regardless of the original shape of the (finite) compressional wave in the medium, a shock front is formed eventually as the wave propagates through the medium. This means that pressure, density, and temperature suffer discontinuous increases in the front of the wave. In the course of its propagation through a medium a pure shock wave decays, this process being superimposed upon the normal weakening of waves due to the geometric factor of divergence, unless mechanical energy is constantly fed into the shock wave. In other words, the mechanical energy of shock waves is being degraded and is then found as the heat energy of the medium after the passage of the wave.

Since a detonation wave is basically a self-sustaining shock wave, a brief qualitative discussion of shock wave formation appears desirable. It is well established that in a compressional wave of finite amplitude the velocity of a portion of a compressional pulse is directly proportional to its amplitude. Those portions of the pulse with the greatest amplitude will travel faster than portions of lower

amplitude, therefore changing the shape of the pulse as indicated in Figure 1.

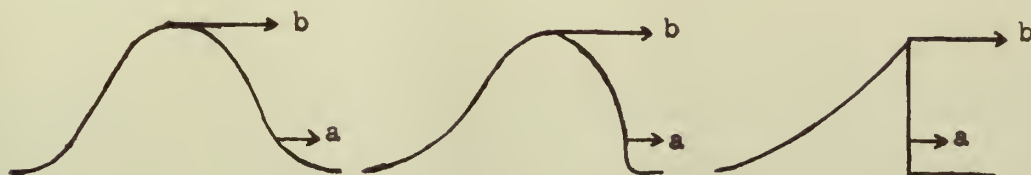


Figure 1

Formation of a Shock Front $P_b > P_a$

Becker's treatment (11) of the origin of a shock wave in a gas is also of interest. Let a piston in a long tube be given a sudden small velocity. The gas in front of the piston will be compressed and a pressure wave will move ahead of the piston with the velocity of sound in the medium. The gas in front of the piston and behind the pressure wave will be moving with the velocity of the piston. If the velocity of the piston is increased by another small increment, a new pressure wave arises that moves somewhat faster than the first, since it moves in the gas already heated by the foregoing compression and moving with the velocity of the piston. Each succeeding wave will move more rapidly than the preceding one and will ultimately overtake the initial one to form a composite wave with an infinitely steep front; i.e., a discontinuity in pressure and temperature will be formed.

The qualitative argument can be made more explicit by the Riemann formulation of the equations of hydrodynamics. Such a treatment is presented by Lamb (12) and the results confirm the conclusions reached above.

By reversing the argument given for compression waves, it is

apparent that a rarefaction wave of finite amplitude, in which the later portions of the wave are regions of lower pressure, will spread out as it advances and a discontinuity will not arise.

Returning to the shock front, which for the purposes of this discussion can be treated as a mathematical plane, it becomes desirable to establish equations relating the conditions on both sides of the discontinuity. The equations for the conservation of mass, momentum and total energy have been employed by Rankine (13) and Hugoniot (10) in the formulation of three conditions relating the pressure, specific volume and particle velocity behind a discontinuity moving with a velocity D to those properties in the undisturbed medium ahead of the discontinuity.

Consider a shock front moving into a region in which the particle velocity is u_0 , the density ρ_0 and the pressure P_0 from a region in which the same properties are denoted by u_1 , ρ_1 and P_1 .

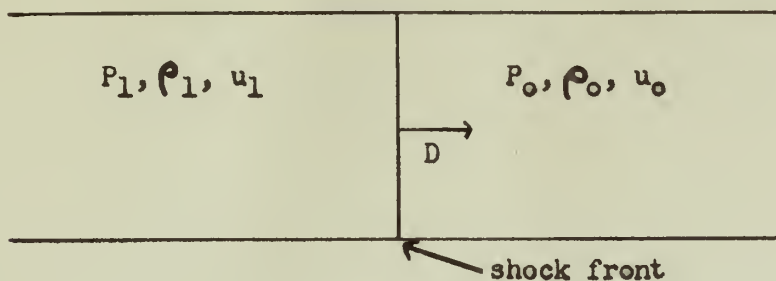


Figure 2

Conditions at a Shock Front Moving with Velocity D .

In a time dt a mass of fluid $\rho_0(D-u_0)dt$ will enter unit cross-section area of the front and a mass $\rho_1(D-u_1)dt$ will leave the front (see Figure 2). As dt is made very small so that the layers on either side are infinitesimal, the mass flow into the front must equal the mass flow away from it. Thus an expression for the conservation of mass may be written:

$$\rho_0(D-u_0) = \rho_1(D-u) \quad (1)$$

The change in momentum associated with the mass flow across the front must equal the net force per unit area. Thus for the conservation of momentum:

$$\rho_0(D-u_0)(u_1-u_0) = P_1-P_0 \quad (2)$$

Finally the conservation of energy requires that the net work done by the pressures P_1 and P_0 equals the increase in kinetic and potential energy. The work done by each pressure is $Pudt$ for unit area, the kinetic energy is $\frac{1}{2} u^2$ and the internal energy is E per unit mass. Therefore,

$$P_1u_1-P_0u_0 = \rho_0(D-u_0) E_1-E_0+\frac{1}{2}(u_1^2-u_0^2) \quad (3)$$

The above equations may be rewritten in the form below by substitution of $V = 1/\rho$ and some algebraic manipulation.

$$D = u_0+V_0 \sqrt{(P_1-P_0)/(V_0-V_1)} \quad (4)$$

$$u_1 = u_0+ \sqrt{(P_1-P_0)(V_0-V_1)} \quad (5)$$

$$E_1-E_0 = \frac{1}{2} (P_0+P_1)(V_0-V_1) \quad (6)$$

The three equations above are often referred to as the Rankine-Hugoniot conditions.

Before proceeding to the consideration of detonation processes, it is desirable to consider Equation 6 in more detail and to investigate the thermodynamic properties of the shock wave. Knowledge of the equation of state and the heat capacity enables one to calculate E_1-E_0 as a function of P_1 and V_1 so that Equation 6 becomes the Rankine-

Hugoniot equation relating the pressure and volume in a compressional wave of finite amplitude for given initial conditions. The relation describes the change in internal energy before and after compression by the shock wave as a function of the pressures and specific volumes. This change is adiabatic, since no heat is exchanged with the surroundings but it is not isentropic. The non-isentropic nature of a shock (or detonation) wave was not appreciated by many of the early investigators and led to a conflict with the energy principle. A method of determining the increase in entropy occurring across a shock front is discussed along with other detonation zone parameters in a later section.

DETONATION WAVES

The existence of detonation waves was originally reported by Berthelot and Vieille (14) in connection with studies of gaseous explosions. Such a wave differs from a shock wave in two respects. In the first place, the wave is sustained and propagated through the mechanism of a chemical reaction supplying energy. Therefore, the chemical energy released must be included in the calculations of the Rankine-Hugoniot conditions. The second difference is that the velocity of the wave is determined by the thermodynamic state of the material immediately behind the wave front rather than by the motion of an external boundary surface as is the case in pure shock waves. The three conditions relating properties of the material on either side of the detonation front in terms of the conservation of mass, momentum, and energy are no longer sufficient to determine the unknown quantities behind the front in addition to the velocity of the front. The problem differs from that considered in the previous section in that there is no controllable external condition, such as the velocity of a piston, available to determine one of the variables behind the front.

The Chapman-Jouguet Condition

An additional relation is required to make possible a unique solution of the hydrodynamic equations. Chapman (15) postulated a relation between the velocity of the detonation wave and the sonic velocity in the gas behind the wave. He also assumed that the minimum detonation velocity consistent with the Rankine-Hugoniot conditions prevailed in a steady detonation. Although his final results were in error due to assuming that isentropic conditions prevailed at a discontinuity,

the basic concept was identical to the mathematical expression published by Jouguet (16) two years later. The condition now bears the name Chapman-Jouguet and postulates

$$D = c_1 + u_1 \quad (7)$$

where u_1 is the material velocity and c_1 the sonic velocity in the reaction products behind the wave front.

Although a valid theoretical proof of the necessity of this condition is not yet available, there is little doubt that it correctly describes the observed phenomenon. Several plausible arguments have been advanced which aid in the acceptance of this condition. The general form of the pressure-volume curve representing possible states of the products after detonation is shown in Figure 3. This curve is specified by the Rankine-Hugoniot conditions, the thermochemical data concerning the explosive and the equation of state.

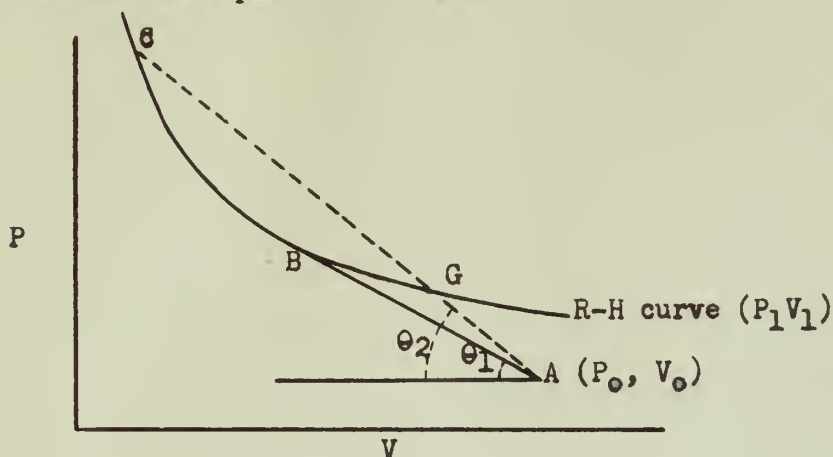


Figure 3

Generalized Rankine-Hugoniot Curve

The point A represents the initial conditions existing in the explosive before the passage of the detonation wave. If the initial

material velocity is zero, as is invariably the case with solid explosives, Equation 4 gives the detonation velocity in terms of the initial and final states.

$$D = V_0 \sqrt{(P_1 - P_0)/(V_0 - V_1)} \quad (8)$$

From Figure 3 it is evident that this relation can be written as

$$D = V_0 \sqrt{\tan \Theta} \quad (9)$$

where Θ is the angle between the system of lines passing through point A and the (negative) V axis. For any value of Θ greater than Θ_1 , there will be two distinct final states (C and G) corresponding to the same value of D. For $\Theta = \Theta_1$, the line AB is tangent to the curve at point B and is the final state corresponding to the minimum value of D.

If the final state of the products corresponds to a point C on the R-H curve higher than the point B, it can be shown (see Appendix A) that the velocity of the detonation wave is less than $u+c$ and a rarefaction wave travelling at sonic velocity with respect to the products would move faster than the detonation and hence engulf and destroy it. (A rarefaction wave will arise from any process that abstracts energy from the reaction products such as heat loss or turbulence.)

At the point B, the velocity of the detonation wave is equal to the velocity of sound in the reaction products plus the mass velocity of those products, thus a rarefaction wave proceeding with its maximum velocity will be unable to overtake the detonation wave. The mathematical proof that $D = c+u$ at point B follows that given by Kistiakowsky and Wilson (17). From Equations 4 and 5 the detonation velocity is given by

$$D = \frac{V_0}{V_0 - V_1} u_1 \quad (10)$$

The velocity of sound in a gas is given by the relation (18)

$$c = \sqrt{(\partial P / \partial \rho)_s} = v \left(-\frac{\partial P}{\partial V} \right)_s^{\frac{1}{2}} \quad (11)$$

If there is a point on the Rankine-Hugoniot (R-H) curve having the same slope as the corresponding point on the isentropic curve (PV curve with constant entropy), then at that point

$$\left(\frac{\partial P}{\partial V} \right)_r = \left(\frac{\partial P}{\partial V} \right)_s$$

where the subscript r refers to the Rankine-Hugoniot curve. Differentiation of the Rankine-Hugoniot relation, Equation 6, holding P_0 and V_0 constant yields

$$dE_1 = -\frac{1}{2}(P_0 + P_1)dV_1 + \frac{1}{2}(V_0 - V_1)dP_1 \quad (12)$$

Now, from the first law of thermodynamics, $dE = TdS - PdV$, thus Equation 12 can be written

$$T_1 \left(\frac{dS_1}{dV_1} \right)_r = \frac{1}{2}(V_0 - V_1) \left[\left(\frac{dP_1}{dV_1} \right)_r - \frac{P_0 - P_1}{V_0 - V_1} \right] \quad (13)$$

It follows that the slope of the R-H curve through a point at which $dS_1 = 0$ can be expressed as shown in Equation 14 below

$$\left(\frac{\partial P_1}{\partial V_1} \right)_r = \left(\frac{\partial P_1}{\partial V_1} \right)_s = \frac{P_0 - P_1}{V_0 - V_1} = -\tan \theta_1 \quad (14)$$

This is also the slope of the line AB which is tangent to the R-H curve at point B. Now the detonation velocity at any point on the R-H curve is given by Equation 4 and is

$$D = V_0 \left(\frac{P_1 - P_0}{V_0 - V_1} \right)^{\frac{1}{2}} \quad (4)$$

Therefore, at point B

$$D = v_0 \left(-\frac{\partial p_1}{\partial v_1} \right)_s^{\frac{1}{2}} = \frac{v_0}{v_1} c_1 \quad (\text{by Eq. 11}) \quad (15)$$

Combining this with Equation 10 yields

$$D = u_1 + c_1$$

The argument which is used to exclude points on the R-H curve below B is based on the entropy of the products. Consider the two points C and G lying on the same straight line from A and corresponding to the same detonation velocity D. The entropy of products at C is greater than at G since the transition from G to C is equivalent to passage from an initial state G across a shock wave of velocity D to the final state C. Since there is a definite increase in entropy accompanying the passage of a shock wave the entropy at C will be greater than at G, therefore the upper point will be a thermodynamically more probable state than G. This is true for all angles of $\theta > \theta_1$.

Thus points above B are more probable than points below but points above B are not stable due to the effect of the rarefaction wave.

The question of the validity of the Chapman-Jouguet condition has also been discussed by von Neumann (19). By applying the conservation Equations 4, 5 and 6 not only to the completely reacted material but also to each stage of the reaction, he has been able to substantiate the validity of the condition in certain cases. In addition to the single R-H curve in Figure 3 representing the final state of the products, there will be a series of R-H curves corresponding to the intermediate stages. Since the detonation velocity is the velocity with which the region of chemical reaction progress, it is the same for each

intermediate stage. Therefore, the line from the initial state P_0, V_0 to each P_{n1}, V_{n1} representing the condition of a given layer must have the same slope and must therefore be the same line for all degrees of completion of the reaction. Since in order to get from incomplete to complete reaction, the material must have traversed all intermediate stages, this line must touch all of the R-H curves corresponding to different degrees of completion. The family of R-H curves corresponding to the degree of completion of the chemical reaction from $n = 0$ to $n = 1$ has the general form shown in Figure 4.

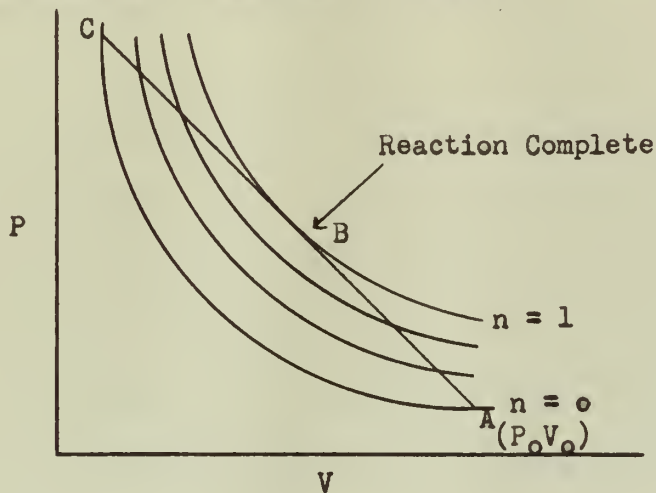


Figure 4

Family of Rankine-Hugoniot Curves from $n = 0$ to $n = 1$.

The motion of a point on the diagram representing the behavior of an element of explosive passing through the shock front and into a finite reaction zone must always remain on a straight line to satisfy the conservation equations. In the shock wave, the representative point must begin on the curve $n = 0$, at point A, must intersect the curves for increasing n in order and finally end somewhere on the curve $n = 1$. In order that there exist a discontinuity in pressure and temperature

at the shock front, there must be another intersection of the straight line with the curve $n = 0$, corresponding to point C. Thus in the shock front the representative point runs from A to the limiting value at the point C where it again meets the curve $n = 0$. So far no chemical reactions have occurred but the explosive material has been "shocked" into a condition where reactions can proceed. Now the representative point must proceed continuously from the curve $n = 0$ to $n = 1$; this requirement immediately restricts the possible intersections to points on $n = 1$ at or above B. If the straight line intersects the curve $n = 1$ at a point above B, the tangent to the curve at that point would be steeper than at B, so the velocity of sound in the products would exceed the detonation velocity, and a rarefaction wave would engulf and destroy the detonation wave. Thus the intersection with the curve $n = 1$ must be at B giving a point of tangency and corresponding to Chapman-Jouguet condition, $D = u_1 + c_1$.

Von Neumann also discusses the case of intersecting R-H curves, but since this possibility does not correspond to any known physical situation it will not be pursued further.

By a straightforward thermodynamic procedure, Scorah (20) has shown that when the Chapman-Jouguet condition is assumed the ratio of entropy increase to available energy passing through the shock front is a maximum. Although this result is in accord with the fundamental principle of maximum degradation of energy observed in natural processes, it is regarded only as a further substantiation of the condition rather than a rigorous proof.

THE DETONATION ZONE

Before proceeding with the development of the fundamental theory, it is advantageous to have an idea of the order of magnitude of the dimensions of the zones in which the process of detonation occurs. The essential elements of a steady one-dimensional detonation process can be illustrated as in Figure 5. The detonation zone is considered to be stationary in space and the explosive feeds into the zone from right to left at the detonation velocity D .

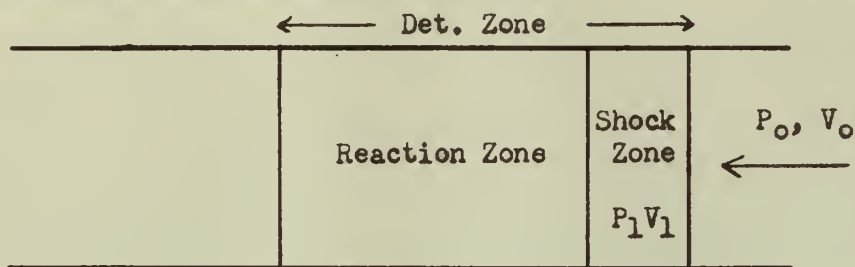


Figure 5

Steady Plane Detonation in a Solid Explosive

Conditions throughout the zone are considered to be steady. The material first passes into a plane shock zone where abrupt increases of pressure, temperature, mass velocity and entropy occur. This transition takes place within a narrow region whose length is determined by the viscosity and the thermal conductivity. If the dimensions of this shock zone are very small in comparison with other lengths under consideration, the shock may be treated as a mathematical plane or discontinuity without error. For one-dimensional motion, the Navier-Stokes equations (21) of motion and energy for a steady state in which the shock wave is at rest are:

$$P - P_0 + \frac{u^2}{V} - \frac{D^2}{V_0} = 4/3\eta \frac{du}{dx}$$

and

$$\Delta E - \Delta Q - \frac{1}{2}(D-u)^2 - P_0(V_0-V) = k \frac{V_0}{D} \frac{dT}{dx}$$

where η is the viscosity, k is the thermal conductivity, u is the material velocity, T is the temperature and x is the coordinate in the direction perpendicular to the shock front. These differential equations have not as yet been solved in closed form for general values of the parameters. For the case of a pure shock wave ($\Delta Q = 0$) in liquid diethyl ether, Becker (22) has calculated the length of the zone to be $6.5A^0$ at a shock pressure of 10,000 atms. and $1.4A^0$ at a pressure of 100,000 atms. For a solid explosive with an assumed viscosity of 0.2 centipose and a thermal conductivity of 10^4 ergs $\text{cm}^{-2} \text{sec}^{-1}$, Eyring (23) calculated the length of the zone to be of molecular dimensions. Calculations including the effects of viscosity and thermal conductivity in the conservation equations have shown these effects to be of importance only at the very front of the detonation wave, where the amount of chemical reaction is negligible.

The distance between the points of initiation of the chemical reaction and the point at which the Chapman-Jouguet condition is applied is called the reaction zone. There are a number of methods for estimating the length of this zone. Since each method rests on the interpretation of a different phenomenon, agreement among results found by different methods greatly enhances the accuracy of the determination. The results of (1) direct observation of the luminous zone, (2) extrapolation of low-temperature rate measurements, (3) surface reaction rate calculations for granular explosives, and (4) studies of the building-up of a low velocity wave to steady state conditions, all indicate that the

reaction zone for TNT under steady state conditions is about $\frac{1}{2}$ centimeter in length. Although the exact figure will vary from explosive to explosive, it is reasonably well established that the reaction zone length for solid explosives is between 1 mm. and 1.5 cm.

The time required for a particle to pass through the reaction zone can be calculated knowing the zone length, detonation velocity, and the material velocity. Reaction times of the order of magnitude of 1 microsecond have been found for practically all organic explosives.

THE HYDRODYNAMIC THEORY

Application of the Rankine-Hugoniot relations and the Chapman-Jouguet condition to an actual chemically supported detonation permits evaluation of the energy relation, Equation 6, in terms of heat of reaction and specific heat data for the reaction products. Since the shock zone is of molecular dimensions any contribution of heat by thermal conduction is neglected. The energy relation can now be written

$$E_1 - E_0 = \frac{1}{2}(P_1 + P_0)(V_0 - V_1) = \frac{Q}{M} + \frac{1}{M} \int_{T_0}^{T_1} C_v dt + \int_{T_1}^V \left(\frac{\partial E}{\partial V} \right) dV \quad (16)$$

or introducing the mean specific heat at constant volume and assuming an ideal gas

$$\frac{1}{2}(P_1 + P_0)(V_0 - V_1) = \frac{Q}{M} + \frac{\bar{C}_v}{M} (T_1 - T_0) \quad (17)$$

where Q is the heat absorbed in the reaction of M grams at the initial temperature T_0 . As indicated above the computation of conditions about the detonation front requires the knowledge of the following:

1. Equation of state of the products
2. Composition of the reaction products
3. Heat capacity of the products
4. Heat of reaction

In the case of solid explosives, the selection of an equation of state for products at temperatures of the order of 3000 - 5000° A and at pressures of 50,000 to 200,000 atmospheres presents a formidable problem. Our present day knowledge of equilibrium constants under the above conditions is also quite meager. In view of this situation, it appears desirable to test the validity of theory under the less stringent conditions provided by gaseous explosions.

Gaseous Explosives

The approach adopted in this discussion is similar to that applied to mixtures of hydrogen and oxygen by Lewis and Friauf (24). Since the equations used for ideal gases will later prove of value in the preliminary treatment of solid explosives, they will be fully developed here. The Rankine-Hugoniot conditions for conservation of mass and momentum, Equations 1 and 2, may be written as below, if u_0 is assumed to be zero.

$$\frac{D}{V_0} = \frac{D-u_1}{V_1} \quad (18)$$

$$\frac{Du_1}{V_0} = P_1 - P_0 \quad (19)$$

Elimination of u_1 from the above equations yields

$$P_1 - P_0 = \frac{D^2}{V_0^2} (V_0 - V_1) \quad (20)$$

At the Chapman-Jouguet point on the R-H curve the detonation velocity expression Equation 4 can be written

$$D = V_0 \sqrt{(P_1 - P_0)/(V_0 - V_1)} = V_0 \sqrt{-(dP_1/dV_1)_s} \quad (21)$$

For an ideal gas, the isentropic expansion law is

$$P_1 V_1^{\gamma_1} = \text{constant}$$

Therefore, differentiating and substituting into Equation 21

$$D = V_0/V_1 \sqrt{\gamma_1 P_1 V_1} = V_0/V_1 \sqrt{\gamma_1 n_1 R T_1 / M} \quad (22)$$

in which n_1 is the number of moles of gas per M grams of product gases. Since the initial pressure P_0 is negligible in comparison with P_1 in

Equation 20, substitution of Equation 20 into Equation 22 with the elimination of D yields

$$\gamma_1 = \frac{v_1}{v_o - v_1} \quad (23)$$

This expression may now be substituted into the energy relation, Equation 17, again neglecting P_o to give

$$\frac{1}{2} \frac{n_1 R T_1}{\gamma_1} = Q + \bar{C}_v (T_1 - T_o) \quad (24)$$

If the chemical reaction under consideration went quantitatively and the distribution of atoms in the products was independent of temperature and pressure, Equation 24 could be solved for the final temperature T_1 if the variation of γ_1 and $\bar{C}_v$ with T were known. Actually, of course, both n_1 and Q depend upon pressure and temperature. The calculation is therefore somewhat more tedious but the principle involved is unchanged.

Once the final temperature is found, the detonation velocity can be computed from the combination of Equations 22 and 23

$$D = (\gamma_1 + 1) \sqrt{n_1 R T_1 / \gamma_1 M} \quad (25)$$

Lewis and Friauf have calculated detonation velocities for mixtures of hydrogen and oxygen with various excesses of both components and with the addition of inert gas. They allowed for the equilibria

$\frac{1}{2} H_2 + O_2 = H_2O$, $H_2 = 2H$, and $H_2O + \frac{1}{2} O_2 = 2OH$. Although the dissociation of O_2 was not considered and no allowance was made for the excess heat capacity of oxygen molecules due to electronic excitation, there is no reason to suggest that a similar calculation undertaken today would differ significantly from their results. The following table shows their calculated values and the experimental results obtained by Dixon

(25) and Payman and Walls (26).

Table I

<u>Mixture</u>	<u>Detonation Velocity</u> D, m/sec		<u>Deviation %</u>
	<u>Computed</u>	<u>Observed</u>	
(2H ₂ +O ₂)	2806	2819	-0.4
(2H ₂ +O ₂) + 1O ₂	2302	2314	-0.7
(2H ₂ +O ₂) + 3O ₂	1925	1922	0.2
(2H ₂ +O ₂) + 5O ₂	1732	1700	2.0
(2H ₂ +O ₂) + 1N ₂	2378	2407	-1.2
(2H ₂ +O ₂) + 3N ₂	2033	2055	-1.1
(2H ₂ +O ₂) + 5N ₂	1850	1822	1.1
(2H ₂ +O ₂) + 2H ₂	3354	3273	2.5
(2H ₂ +O ₂) + 4H ₂	3627	3527	2.8
(2H ₂ +O ₂) + 6H ₂	3749	3532	6.1

The agreement between the calculations and the observed measurements serves as an extremely good verification of the hydrodynamic-thermodynamic theory. With one exception the differences between the comparative values are all within the experimental errors of velocity measurements. The detonation velocity of a number of gaseous explosives of the hydrocarbon-oxygen type also have been calculated and found to be in good agreement with experimentally determined values.

Solid Explosives

The extension of the fundamental theory to the detonation of solid explosives requires the selection of an equation of state applicable to gases under extreme conditions of temperature and pressure. Use of the ideal gas law is immediately ruled out since the experimentally observed detonation velocities are quite sensitive to initial density and Equation 25 based on the ideal gas law shows no dependence on this factor.

Another complicating factor arising with solid explosives is

the question of the composition of the reaction products. To consider all of the various equilibria possible when a typical explosive containing atoms of carbon, hydrogen, nitrogen and oxygen detonates is a tremendous mathematical task and cannot be justified in view of the uncertainty of the thermodynamic functions of the possible products. Justification for ignoring the more complicated equilibria involving free atoms, polyatomic molecules and free carbon in approximate computations will be presented later.

Variation of Parameters - Abel Equation of State

To illustrate the form assumed by the hydrodynamic equations and to ascertain certain qualitative aspects of the process of detonation a particularly simple equation of state will be chosen as an example. An equation suitable for this purpose, but of less value in connection with practical calculations, is the Abel equation, $P(V - \alpha) = RT$, with the covolume α assumed constant.

The details of deriving the relations will for the most part be omitted. The derivations are quite straightforward and similar to those given by Eyring and his associates (7).

Evaluation of the sonic velocity appearing in the Chapman-Jouguet conditions, Equation 7, in terms of the equation of state yields

$$(D - u_1)^2 = v_1^2 \gamma \frac{P_1}{v_1 - \alpha} \quad (26)$$

which when inserted into the Rankine-Hugoniot relations and combinations of these relations gives the following five equations. (The initial pressure P_0 is negligible in comparison to P_1 and is omitted.)

$$\frac{V_1}{V_0} = \frac{\gamma + \alpha/V_0}{\gamma + 1} \quad (27)$$

$$P_1(V_0 - \alpha) = 2R \frac{Q + \bar{C}_v T_0}{\bar{C}_v} \quad (28)$$

$$T_1 = \frac{Q + \bar{C}_v T_0}{\bar{C}_v} \frac{2\gamma}{\gamma + 1} \quad (29)$$

$$D^2 = (Q + \bar{C}_v T_0) \frac{2(\gamma^2 + 1)}{(1 + \alpha/V_0)^2} \quad (30)$$

$$\frac{u_1}{D} = \frac{\gamma + \alpha/V_0}{\gamma + 1} \quad (31)$$

Equations 27 to 31 furnish the detonation velocity and all other properties of the reaction products provided we have data concerning the heat of reaction, the mean heat capacity of the products, the covolume and the gas constant per gram. It is apparent that neither the detonation velocity nor any of the properties of the products depend upon the rate of chemical reaction.

An estimate of the probable accuracy of the calculated properties can be made from the above equations. The final temperature is a function of the heat of reaction and the mean heat capacity of the products and in particular is independent of the covolume; thus the temperature should be determinable to a higher accuracy than properties depending on additional data. In particular the final pressure is least accurately obtained since, in addition to dependence upon the thermal

data and the covolume, it is also a function of the gas constant which depends upon the mean molecular weight of the products.

The properties of the reacting explosive can be determined at various intermediate stages by replacing Q in Equations 27 to 31 by nQ where n denotes the degree of completion of the reaction. It is interesting to note that such a procedure is another application of the mechanism used by von Neumann in his attempt to justify the selection of the Chapman-Jouguet condition based upon the family of Rankine-Hugoniot curves. The variation of the properties, temperature, pressure, ratio of $c+u$ to D and entropy of a typical explosive as the reaction proceeds is indicated in Figure 6. Each property is plotted in terms of percent of the final value.

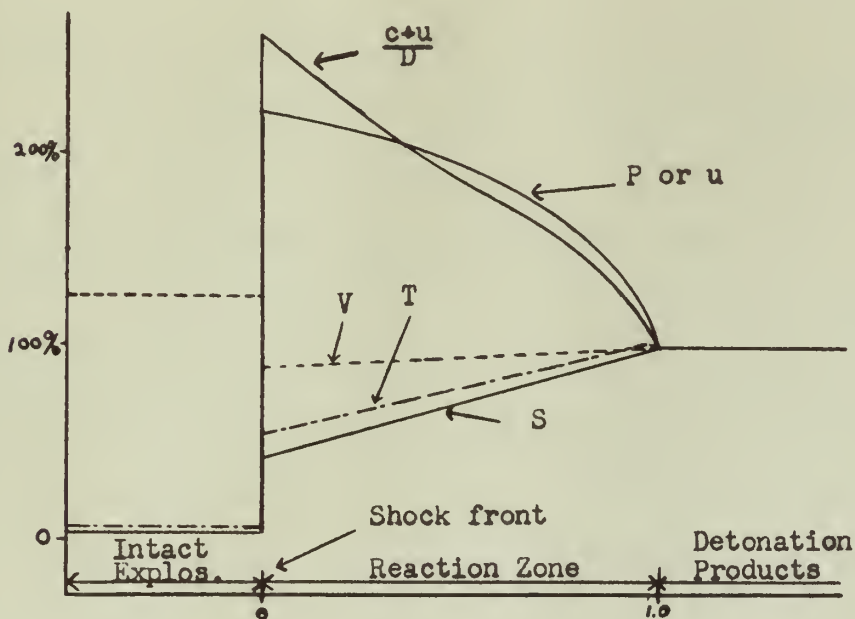


Figure 6

Variation of Properties within the Detonation Zone.

At the shock front the pressure is twice the value attained at the end of the reaction zone, since the substitution of nQ into Equation 28 and simplifications yields, to close approximation, the relation

$$P_n \approx (1 + \sqrt{1-n})P_1$$

The mass velocity u_n is always the same fraction of its final value as is the pressure P_n ; therefore, the same curve represents the variation of both parameters through the reaction zone.

The ratio of $(c+u)$ to D exceeds 2 at the shock front and reaches unity at the end of the reaction zone, thus it is seen that within the reaction zone a rarefaction wave of velocity $c+u$ will continually overtake and decrease the velocity of a discontinuity progressing at a lower velocity. At the end of the reaction zone $D = c+u$, (the Chapman-Jouguet condition) and a stable detonation wave is possible.

The temperature and entropy show sharp increases at the shock front and a gradual rise throughout the reaction zone.

Equation of State Based on Energy Considerations

In order to improve the agreement between calculated and observed values of the detonation velocity, equations of state more representative of the extreme conditions confronted have been suggested. Jones (27) has developed an equation suitable for use at high pressures based upon Bridgman's (28) results with nitrogen at pressures up to 15,000 atmospheres. The equation takes the form

$$P = RT f\left(\frac{V}{N}, T\right) - \frac{dE_0(V/N)}{d(V/N)}$$

where $E_0(V/N)$ is assumed to be the potential energy of interaction of

molecules in the gaseous product and N is the number of moles. The internal energy E_0 is expressed in the form

$$E_0(V/N) = Ae^{-\alpha V/N} + B(V/N) + C$$

in which the first term represents the repulsive forces and the second the attractive forces. The constant C is assigned a value to make the minimum energy equal to the heat of vaporization. The function f is evaluated from compressibility data and the constants A , B and α from the energy of the normal modes of vibration of molecules in the fully excited solid state.

At lower temperatures, Jones assumes an equation of the virial form, the constants being adjusted so that the pressure computed at an intermediate value of V by the both relations is the same. Extending the interaction effects determined by Bridgeman to higher temperatures and densities the total energy of the reaction products can be expressed as

$$E = \sum [N_i E_i + (\sum N_i - N_s)(E_0 + 3/2RT)]$$

where N_i is the number of moles of each molecular species, both gas and solid, E_i is the energy per mole exclusive of the interaction of molecules in the gas phase and N_s is the number of moles of solid products. The last term, therefore, accounts for the energy of molecular interaction plus the vibration energy of $3/2RT$ per mole. The energies E_i can be evaluated from specific heat data at ordinary pressures since the interaction effects at high pressures are represented by E_0 . To determine the composition of the reaction products as a function of temperature, the activities of the various products are introduced.

The activity of each species can be expressed in terms of the composition N_i and the equilibrium constants for the assumed reactions as a function of temperature at normal pressures to which ideal gas conditions are applicable. The increase in internal energy of the products must be the sum of the chemical energy Q released by the reaction and the work done by the pressure at the detonation front. Thus a knowledge of E , Q and the equation of state provides sufficient information to solve the detonation front equations.

Although the above procedure involves several major assumptions to make it feasible, the calculation is significant because the results tabulated in Table III give an idea of the success obtainable using an equation of state fitted to data other than that obtained by detonation measurements.

The Halford-Wilson-Kistiakowsky Equation of State

Information on gas states at the pressures and temperatures encountered in detonations can be obtained by the use of the hydrodynamic theory if the variation of detonation velocity is known as a function of the initial specific volume (loading density). Since the detonation velocities of solid explosives show a definite increase with loading density, such measurements provide a suitable means for finding the deviations of explosion gases from ideal gas behavior. The detonation velocity-loading density relationship is of little value in suggesting the correct form of an equation of state, but, once a form is established, the relationship is sufficient for the quantitative evaluation of its empirical parameters. Unfortunately, the pressure-volume relationship is rather insensitive to the form chosen which suggests the measurement

of detonation temperature for determining the appropriateness of the choice. Since detonation temperatures have not as yet been determined to a degree of accuracy sufficient to provide a check, we are forced to accept the form which fits the data best in the largest number of cases.

An equation of state found to be very successful in the calculation of detonation velocities is one developed by R. S. Halford in cooperation with Wilson and Kistiakowsky (17). The equation of state has the following form when all the products of reaction are gaseous

$$PVM = nRT(1 + \sum e^{\beta X_i}) \quad (32)$$

with
$$X = \sum n_i k_i / T^{\alpha} V M$$

V is the specific volume, n is the number of moles of gas per M grams; P, T and R are the pressure, temperature and the gas constant per gram mole, respectively; and n_i and k_i are the number of moles and an empirical "covolume" parameter of the i-th species, respectively; the summation extends over all gas species present. Satisfactory results have been obtained with the constants $\alpha = 0.25$ and $\beta = 0.30$.

In cases in which solid products are formed in the detonation, the equation is slightly modified. It is assumed that the volumes of gas and solid are additive and that the gas obeys Equation 32 independent of the presence of solid components. Since thermal expansion and baric compression of solids have opposing effects in respect to the volume, and since these effects are not known at the elevated temperatures and pressures encountered, it is assumed that the specific volume of a solid component is independent of temperature and pressure. Thus the specific volume of solid components may be assigned values determined under normal conditions or may be treated as adjustable parameters. With these

assumptions, the equation of state for a mixture of solid and gaseous components becomes

$$PM(V-V_s) = nRTF(x) \quad (33)$$

where V_s is the volume of solid constituents per gram of mixture, obtained by

$$V_s = \eta_a V_a + \eta_b V_b + \dots \quad (33a)$$

$\eta_a, \eta_b, \dots$ are the weight fractions and $V_a, V_b, \dots$ are the specific volumes of solid constituents a, b, ... $F(x)$ is a function defined by

$$F(x) = 1 + xe^{\beta x} \quad (33b)$$

with

$$x = k/T^\alpha M(V-V_s) \quad (33c)$$

$$k = \sum n_i k_i \quad (33d)$$

The value of α and β and all other symbols are the same as those used with Equation 32. A theoretical evaluation of the covolume factors (c.f. Equation 33d) is impractical in view of the extremely high density encountered in the reaction zone. These factors are therefore determined by comparison of the results of a calculation of detonation velocity based on an assumed value with the actual observed velocity. As an initial approximation only the most abundant detonation products are considered and the total covolume constant k of the mixture is obtained for several explosives at a number of loading densities. To evaluate the specific covolume factors k_i , it is assumed that k is an additive function of specific values. The individual values are then adjusted by an iterative procedure for optimum conformance with the mixture values.

Since the original work was completed, other methods of evaluating these constants have been suggested and a wider range of explosives has been used as a basis, yielding slightly modified values. It has been found that the calculation of product composition is much more sensitive to the individual values of k_1 than is detonation velocity.

The application of the Halford-Wilson-Kistiakowsky equation of state to the calculation of detonation velocities and related quantities will be illustrated below.

CALCULATION OF THE DETONATION VELOCITY AND RELATED QUANTITIES

The calculation of the detonation velocity and related quantities using the Halford-Wilson-Kistiakowsky equation of state takes into account the effects of gas imperfections and results in an entirely acceptable set of parameters in the vast majority of explosives to which it has been applied.

Calculation of Detonation Velocity

From pure thermodynamics, we obtain the relation

$$\left(\frac{dP}{dV}\right)_s = -\left(\frac{dP}{dT}\right)_v \left(\frac{dT}{dS}\right)_v \left(\frac{dS}{dT}\right)_p \left(\frac{dT}{dV}\right)_p = \gamma \left(\frac{dP}{dV}\right)_t \quad (34)$$

Differentiating the equation of state, Equation 33, holding T constant gives the result

$$\left(\frac{dP}{dV}\right)_t = -\frac{P(1+2xe^{\theta x} + \theta x^2 e^{\theta x})}{(V-V_g)(1+xe^{\theta x})} \quad (35)$$

From Equation 33b, the coefficient of $(V-V_g)$ can be represented by $F(x)$ and that of P by $y(x)$ where

$$y(x) = F(x) + \frac{x dF(x)}{dx} \quad (36)$$

Thus Equation 35 can be written

$$\left(\frac{dP}{dV}\right)_t = -\frac{Py(x)}{(V-V_g) F(x)} = \frac{1}{\gamma} \left(\frac{dP}{dV}\right)_s \quad (37)$$

Substitution into the basic equation for D, Equation 21, yields the expression

$$D = V_o \sqrt{P_1 \gamma_1 y(x_1) / (V_1 - V_g) F(x_1)} \quad (38)$$

Introducing the equation of state once again gives

$$D = \frac{V_o}{V_1 - V_s} \sqrt{\gamma_1 n_1 R T_1 y(x_1) / M} \quad (39)$$

Equation 38 may be substituted into Equation 4 to obtain an expression in terms of the specific volumes (P_o is neglected)

$$P_1 = \frac{P_1 y(x_1)}{F(x_1)} \frac{\gamma_1 (V_o - V_1)}{(V_1 - V_s)} \quad (40)$$

which on rearrangement becomes

$$\frac{V_o - V_s}{V_1 - V_s} = \frac{1 + F(x_1)}{y(x_1) \gamma_1} \quad (41)$$

Calculation of the Specific Heat Ratio

From thermodynamics, one obtains the following equations for the specific heat at constant volume and the ratio of the specific heats at constant pressure to that at constant volume

$$C_v = C_v^* + MT \int_{\infty}^{V - V_s} (d^2P/dT^2)_v dV \quad (42)$$

where C_v^* is the ideal heat capacity per M grams and

$$\gamma = 1 - \frac{TM}{C_v} \left(\frac{dP}{dT} \right)_v^2 \bigg/ \left(\frac{dP}{dV} \right)_t \quad (43)$$

Introducing the equation of state in these expressions yields

$$C_v = C_v^* + nR \alpha(z(x) - 1) \quad (44)$$

$$\text{and } \gamma = 1 + nR \left[\overline{z(x)^2} / C_v y(x) \right] \quad (45)$$

$$\text{where } z(x) = F(x) - \alpha x \frac{dF(x)}{dx} \quad (46)$$

Calculation of the Temperature

For an imperfect gas, Equation 16 expresses the application of the first law of thermodynamics

$$M(E_1 - E_0) = Q + \bar{C}_V^* (T_1 - T_0) + M \int_{\infty}^{(V_1 - V_s)} (dE/dV)_{T_1} dV \quad (47)$$

(The reaction is first carried out to the final temperature at a large volume, such that the product gases are ideal, and these gases are then compressed to their final volume with a resultant energy term due to the gas imperfections.)

Introducing the equation of state and standard thermodynamic relations, one obtains

$$M \int_{\infty}^{(V_1 - V_s)} (dE/dV)_{T_1} dV = n_1 RT_1 \alpha(F(x_1) - 1) \quad (48)$$

Equation 41 can be rearranged to the form

$$V_0 - V_1 = \frac{F(x_1) (V_1 - V_s)}{y(x_1) \gamma_1} \quad (49)$$

which when combined with the Hugoniot Equation 6 yields

$$E_1 - E_0 = \frac{1}{2} P_1 F(x_1) V_1 / y(x_1) \gamma_1 = \frac{1}{2} n_1 RT_1 F^2(x_1) / y(x_1) \gamma_1 M \quad (50)$$

Therefore, from Equations 47, 48 and 50, one obtains

$$T_1 = \bar{C}_V^* T_0 - Q / \bar{C}_V^* + n_1 R \alpha(F(x_1) - 1) - n_1 R F^2(x_1) / 2y(x_1) \gamma_1 \quad (51)$$

Solution of the above equations is based on an assumed knowledge of the final composition, thus an iterative approach appears desirable. If a large number of explosives are to be investigated a two-stage method is recommended. This involves the calculation of ideal values of D , T , and γ based on the assumption that the product gases are ideal and then

evaluating the ratio of actual to ideal values using tables prepared for this purpose.

The entropy increase occurring in the detonation zone can be estimated if values for the increase in temperature and volume across the shock wave are assumed.

The entropy increase across the shock zone due to an irreversible compression to a pressure P and temperature T is given by

$$\Delta S = C_v \ln \frac{T}{T_0} + \frac{(\partial V / \partial T)_P}{(\partial V / \partial P)_T} (V_0 - V_1) \quad (52)$$

The entropy change due to the irreversible chemical reaction can be calculated by proceeding from the initial to the final state by hypothetically reversible steps, applying the relation

$$\Delta S = S^{\circ}_{\text{Prod.}} - S^{\circ}_{\text{Explos.}} + n C_p \ln \frac{T_1}{T_0} - n R \ln \frac{P_1}{P_0} \quad (53)$$

in which the subscript 1 refers to the conditions prevailing at the end of the reaction zone.

COMPOSITION OF THE DETONATION PRODUCTS

In order to carry out calculations of the detonation velocity and other parameters of interest, it is necessary either to calculate the equilibrium composition of the reaction products or to make an assumption regarding this composition. Before discussing the detailed methods used to determine the composition, a few general remarks concerning equilibria among possible products appear desirable.

Dissociation into free atoms and radicals is fortunately not of importance at the high pressures encountered in detonation of solid explosions. The dissociation constant of $H_2 = 2H$ at $5000^\circ K$ has been calculated statistically to be 44.7 atm. Since the concentration of hydrogen gas rarely exceeds 10% by volume in most explosives, it is found that at a pressure 10^5 atmospheres about 2% of the hydrogen is dissociated into atoms. This corresponds to an absorption of heat of about 3 kilocalories per kilogram of explosive, whose total heat of explosion is of the order of 1000 kcal. per kg. Thus, the final temperature is lowered to the extent of 0.3% by the inclusion of this dissociation but at the same time, the number of moles of products and the pressure is increased. The two effects oppose each other as far as detonation velocity is concerned and it is estimated that the net effect results in a 0.10% decrease in the velocity. The dissociations of O_2 and N_2 occur to a much lesser extent and can also be ignored in all calculations. Although the dissociations of water: $H_2O = \frac{1}{2} H_2 + OH$ and $H_2O = \frac{1}{2} O_2 + H_2$ take place to only a very small extent these equilibria are considered in precise calculations.

Various polyatomic molecules have been detected in gas samples

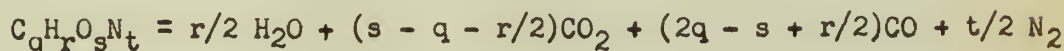
analyzed after closed bomb detonations. Schmidt (29) has reported small but variable amounts of CH_4 , NH_3 , C_2H_2 , HCN and C_2N_2 from almost all explosives. It is suspected that the majority of these molecules are formed after the detonation is complete and while the products are cooling. Allowance is made in precise computations for the formation of methane and ammonia, but the remaining three are neglected in the interest of mathematical simplification. If it is assumed that the analytical data represents the true conditions existing in the detonation wave, the formation of all these complex molecules has a small but not negligible effect on the results of calculation. For example, in TNT where the oxygen deficiency is large and the polyatomic molecules listed above are particularly abundant neglecting their formation results in an overestimation of the detonation velocity by about 3.5%.

The formation of free hydrogen in absence of solid carbon is considered in precise computations even though the equilibrium constant of the "water-gas" reaction, $\text{H}_2\text{O} + \text{CO} = \text{CO}_2 + \text{H}_2$ ranges from 0.2 at 3000° to 0.07 at 5000°K . Since the number of moles of products does not change the only effect on the calculations is that due to the evolution of heat. The neglect of this equilibria in the absence of solid carbon can result in an underestimation of the rate by only a few percent. If, on the other hand, free carbon is present, the reaction $\text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2$ proceeds almost quantitatively. The equilibrium constant of this reaction is of the order of 10^5 atm. at 3000° and 10^6 atm. at 5000°K . Since the fugacity of CO in the reaction zone is usually less than 10^5 atm., the ratio $f_{\text{H}_2}/f_{\text{H}_2\text{O}}$ is greater than unity as long as carbon is present. The assumption that the reaction goes completely to the right results in

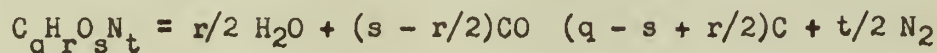
an overestimation of the detonation rate since the heat absorption is overcompensated for by an increase in the number of moles of gaseous products.

As a first approximation results may be obtained using the following arbitrary decomposition equations for explosives of the general formula, $C_qH_rO_sN_t$.

Case A: $(q + r/2 \leq S)$



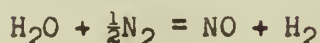
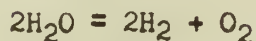
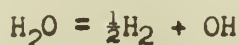
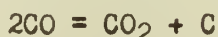
Case B: $(q + r/2 \geq S)$



These equations express the assumption that all the hydrogen is converted to water, that the remaining oxygen then converts carbon to carbon monoxide and that additional oxygen, if any, converts carbon monoxide to carbon dioxide. The results of a calculation using the arbitrary product composition given by the above equations are shown in Table III.

If one assumes that the detonation products are in chemical equilibrium at the final temperature pressure and density, then the equilibrium relations together with the stoichiometric restrictions provide the necessary relations for the calculation of the product composition. The thermodynamic equilibrium constants for the significant equilibria can be computed from the function $-(F^0 - E_0^0)/T$ for each of the components, together with ΔE_0^0 for the equilibria of interest. Tables of these quantities for H_2 , CO , CO_2 , H_2O , N_2 , OH , O_2 , and NO and for the following equilibria over the temperature interval, 2000° -

5000°K. have been published (30).



The problem is conveniently approached by the consideration of the work content A of M grams of a mixture of gases at a large volume V^0 and temperature T_1 . From the thermodynamic relations, we have

$$A(V^0, T_1) = \sum n_i \mu_i^0 + RT_1 \ln \pi (p_i^0)^{n_i} - nRT_1 \quad (54)$$

where n_i is the number of moles of the i -th constituent and μ_i^0 and p_i^0 are its chemical potential and partial pressure, respectively, in the standard state (pure i -th component at T_1 and unit pressure). n is the total number of moles.

Equation 54 can be written

$$A(V^0, T_1) = \sum n_i \mu_i^0 + RT_1 [n \ln P/n + \sum n_i \ln n_i - n] \quad (55)$$

The work content at a volume V_1 is obtained by

$$A(V_1, T_1) = A(V^0, T_1) - M \int_{V^0}^{V_1} P dV \quad (56)$$

To evaluate the integral requires the introduction of an equation of state. Since calculations reported in a later section have been based on the Halford-Wilson-Kistiakowsky equation, Equation 33, this will be used. To simplify the resulting expression it is convenient to use the function $F(x)$ as defined in Equation 33b. Performing the indicated

integration and simplifying one obtains

$$A(V_1 T_1) = \sum n_i \mu_i^0 + RT_1 \left\{ n_i \ln n_i + n \ln \left[P_1 / n F(x_1) \right] \right. \\ \left. n(e^{\beta x} - 1) / \beta - n \right\} \quad (57)$$

The chemical potential is given by

$$\mu_1 = \left(\partial A / \partial n_1 \right)_{T_1 V_1 n} \quad (58)$$

and therefore

$$\mu_1 = \mu_1^0 + RT_1 \left[\ln n_1 + \ln(P_1/n) + 2.303 \Gamma_1(x_1) + \right. \\ \left. 2.303 n k_1 \Gamma_2(x)/k \right] \quad (59)$$

$$\text{where } \Gamma_1(x) = 0.4343 (e^{\beta x} - 1) / \beta - \log F(x) \quad (60)$$

$$\Gamma_2(x) = 0.4343 x e^{\beta x} \quad (61)$$

These functions have been tabulated with x as the argument (31). The chemical reaction may be represented by

$$\sum W_{ji} x_i = 0 \quad (62)$$

where the mole number W_{ji} for the i -th constituent in the j -th reaction is taken positive for products and negative for reactants. Thus

Equation 59 may be written

$$\sum W_{ji} \mu_i = \sum W_{ji} \mu_i^0 + RT_1 \left[\sum W_{ji} \ln n_i + \sum W_{ji} (\ln(P_1/n) + \right. \\ \left. 2.303 \Gamma_1(x_1) + 2.303 n \sum W_{ji} k_1 \Gamma_2(x)/k \right] \quad (63)$$

Now, since at equilibrium $\sum W_{ji} \mu_i = 0$ and by definition $\sum W_{ji} \mu_i^0 = -RT \ln K_{pj}$ we may write

$$\log K_{pj} = \sum W_{ji} \log n_i - \log G_j \quad (64)$$

where K_{pj} is the thermodynamic equilibrium constant for the j -th reaction

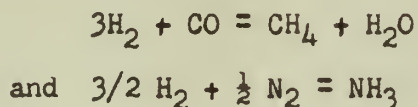
and the quantity G_j is defined by the equation

$$-\log G_j = \frac{\left[\log(P_1/n) + \sum_1 (x_1) \right] \sum_{W_{ji}} + n \sum_2 (x_1)}{\sum_{W_{ji}} k_1/k} \quad (65)$$

Thus one can now write for the equilibrium constant in terms of moles (K_j)

$$K_j = K_{p_j} G_j = \prod (n_i)^{W_{ji}} \quad (66)$$

If there are l constituents in the mixture, composed of m different atomic species, there will be $(l - m)$ relations of the form of Equation 66 and m stoichiometric relations. A convenient iterative procedure and the tabulated functions necessary for the calculation of the equilibrium composition of the reaction products are available in reference (31). The equilibria usually considered include the five equations given above as well as



A comparison of the final composition of some typical explosives based upon the arbitrary decomposition equation and the equilibrium considerations is given in Table II below. The composition is given as the number of moles of each constituent per mole of explosive.

Table II

	TNT $P_0 = 1.0$		Tetryl $P_0 = 1.0$		Cyclonite $P_0 = 1.3$	
	Arbit.	Equil.	Arbit.	Equil.	Arbit.	Equil.
H ₂	0	0.09	0	0.08	0	0.02
CO ₂	0	0.18	0	0.24	0	0.16
CO	3.5	3.38	5.5	5.27	3.0	2.78
H ₂ O	2.5	2.26	2.5	2.24	3.0	2.87
N ₂	1.5	1.46	2.5	2.45	3.0	2.96
NO	0	0	0	0	0	0.02
CH ₄	0	0.01	0	0.01	0	0
NH ₃	0	0.09	0	0.10	0	0.07
C	3.5	3.43	1.5	1.48	0	0.06
OH	0	0	0	0.01	0	0.01

Comparison of product composition, based upon arbitrary and equilibrium relations.

RESULTS OF THE CALCULATIONS

Table III is an example of the results obtained by Brinkley and Wilson (31) using the method of approach discussed in the previous section. The initial and final densities, ρ_0 and ρ_1 , are in grams/cubic centimeter. The detonation velocity, D , and the mass velocity, u_1 , are in meters per second. The temperature is in degrees Kelvin and the pressure in kilobars (10^9 dynes/cm²). The composition is in gram moles of the individual constituent per gram mole of explosive.

A tabulation of the results obtained by Jones (27) using TNT $\rho_0 = 1.5$ is included for comparison. Jones' final composition gives larger values for CO₂ and CH₄ at the expense of H₂O and CO. The available experimental data on detonation product composition indicate much smaller quantities of methane, however, it is entirely possible that formation may have occurred during the cooling process. The equilibrium of reactions involving CO and CO₂ are also sensitive to temperature changes. On the whole, it is reasonable to suppose that the compositions given by the Brinkley-Wilson procedure are a closer approach to the actual conditions. This is also suggested by the better agreement with the observed (32) detonation velocity of 6620 meter/sec. for an initial density of 1.5.

The right-hand column contains results based on the arbitrary decomposition equations. It appears that the detonation velocity, which is the only property that can be measured accurately, is comparatively insensitive to the composition. Although the three methods give results of the same order of magnitude, it is felt that the equilibrium approach of Brinkley and Wilson is preferable.

A comparison of observed and calculated detonation velocities of some common explosives is shown in Figures 7, 8 and 9. The observed velocities are those reported by the Explosives Research Laboratory (32), Bruceton, Pa. The calculated values are based on the method of Brinkley and Wilson with consideration of the seven primary equilibria. The overall agreement is considered to be very good.

Deviations may be due to errors in the observed quantities, however, these are usually accurate to within 3 - 4%, or to errors in the heat of formation of the explosive or to inadequacies of the method due to lack of accurate data in regard to covolume factors and equilibrium constants under the extreme conditions.

The heats of formation of the explosives considered in Figures 7, 8 and 9 are based on the values reported by Schmidt (33) in 1924.

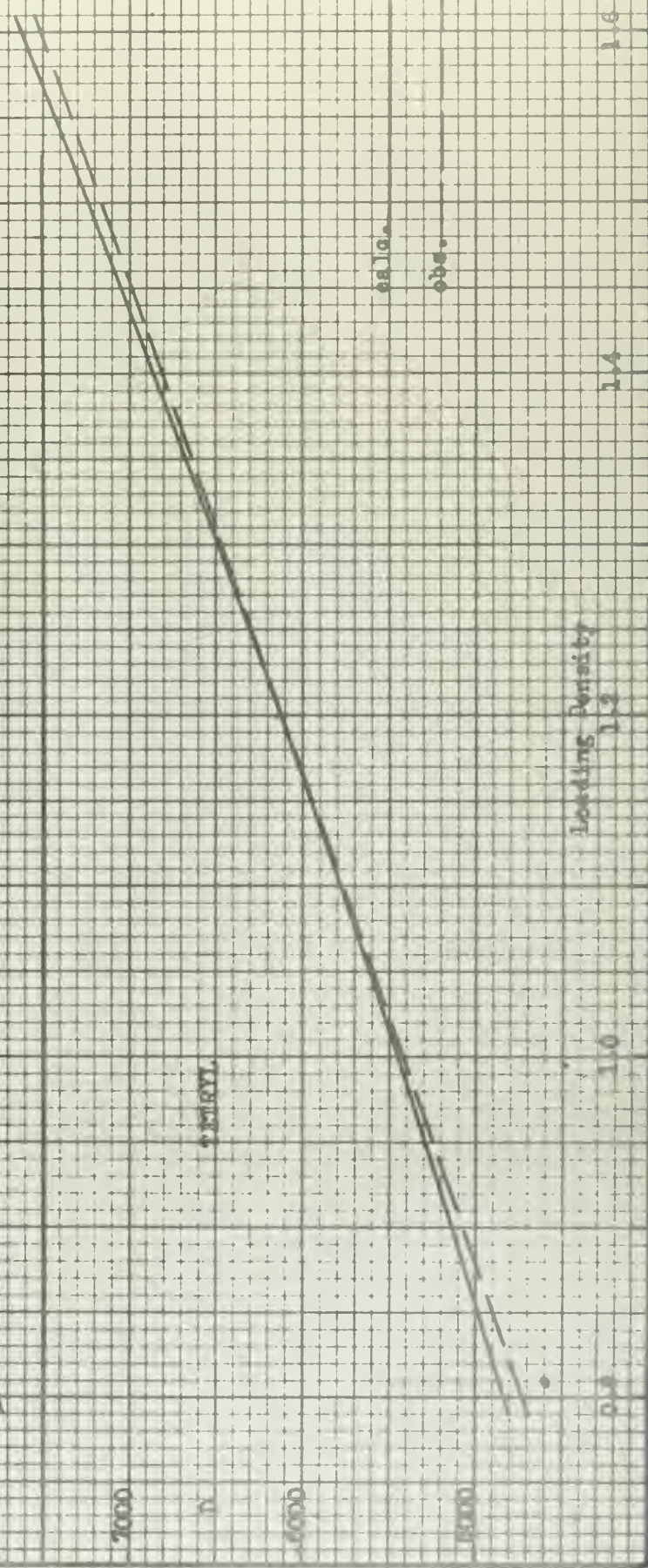
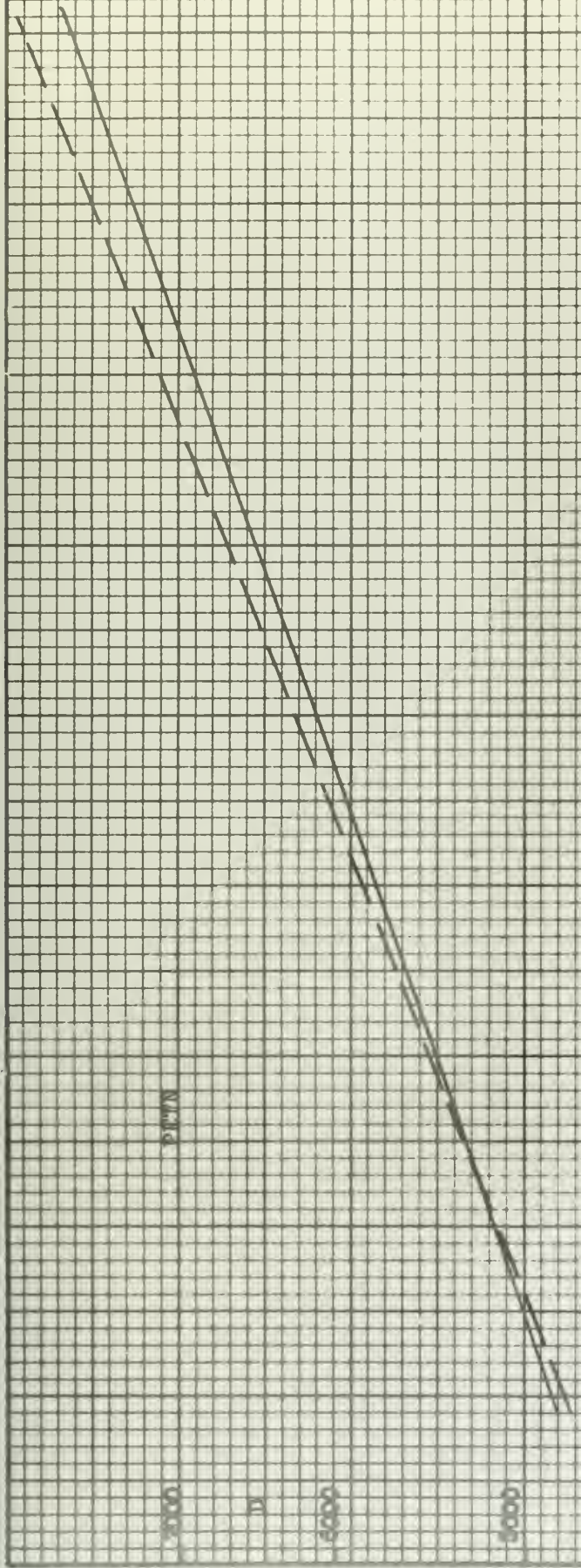
Table III

Calculated Values of the Detonation Velocity
and of the Properties of the Detonation Wave

	TNT							*	**
P_0	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.5	1.6
P_1	1.347	1.464	1.578	1.690	1.801	1.911	2.019	1.94	
D	4870	5190	5540	5920	6340	6820	7290	7720	7210
U_1	1250	1290	1330	1370	1410	1460	1510	1750	
T_1	3260	3270	3270	3240	3210	3190	3170	3460	2880
P_1	61.0	73.6	88.6	105.0	125.4	151.6	177.8	205	173
Composition									
H ₂	.09	.05	.02	.01	0	0	0	0	0
CO ₂	.18	.21	.25	.31	.38	.46	.54	2.64	0
CO	3.38	3.22	3.08	2.92	2.75	2.58	2.42	.06	3.5
H ₂ O	2.26	2.36	2.42	2.46	2.48	2.48	2.48	1.10	2.5
N ₂	1.46	1.47	1.48	1.49	1.49	1.48	1.48	1.50	1.5
NO	0	0	0	0	.01	.02	.02	0	0
CH ₄	.01	0	0	0	0	0	0	.70	0
NH ₃	.09	.06	.04	.02	.01	.01	.01	0	0
C	3.43	3.57	3.67	2.77	3.87	3.96	4.04	3.84	3.5

* Based on Jones' equation of state.

** Based on arbitrary decomposition equations.



PICRIC ACID

7000

η

5000

5000

AMMONIUM PICRATE

7000

η

5000

5000

Loading Density

1.2

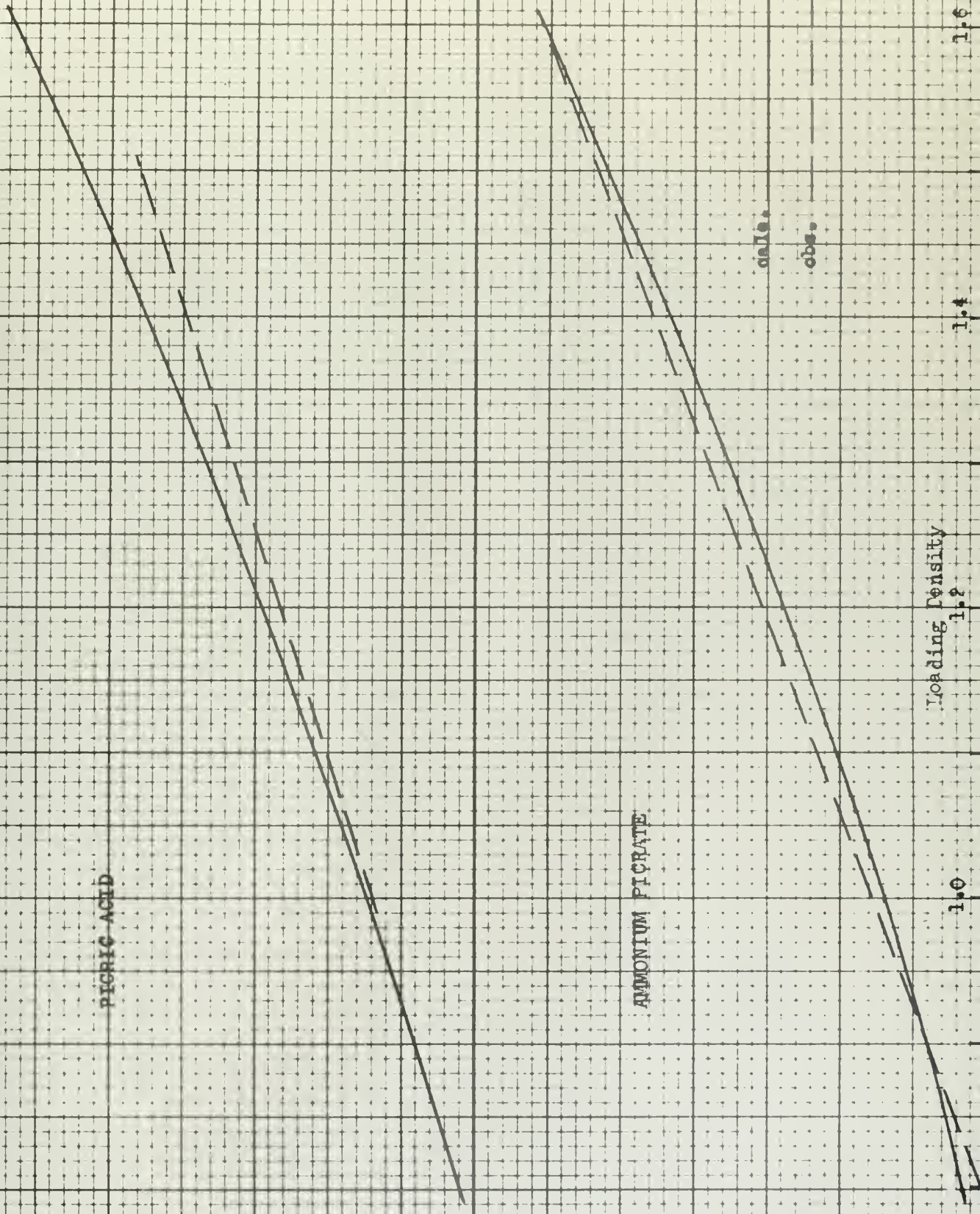
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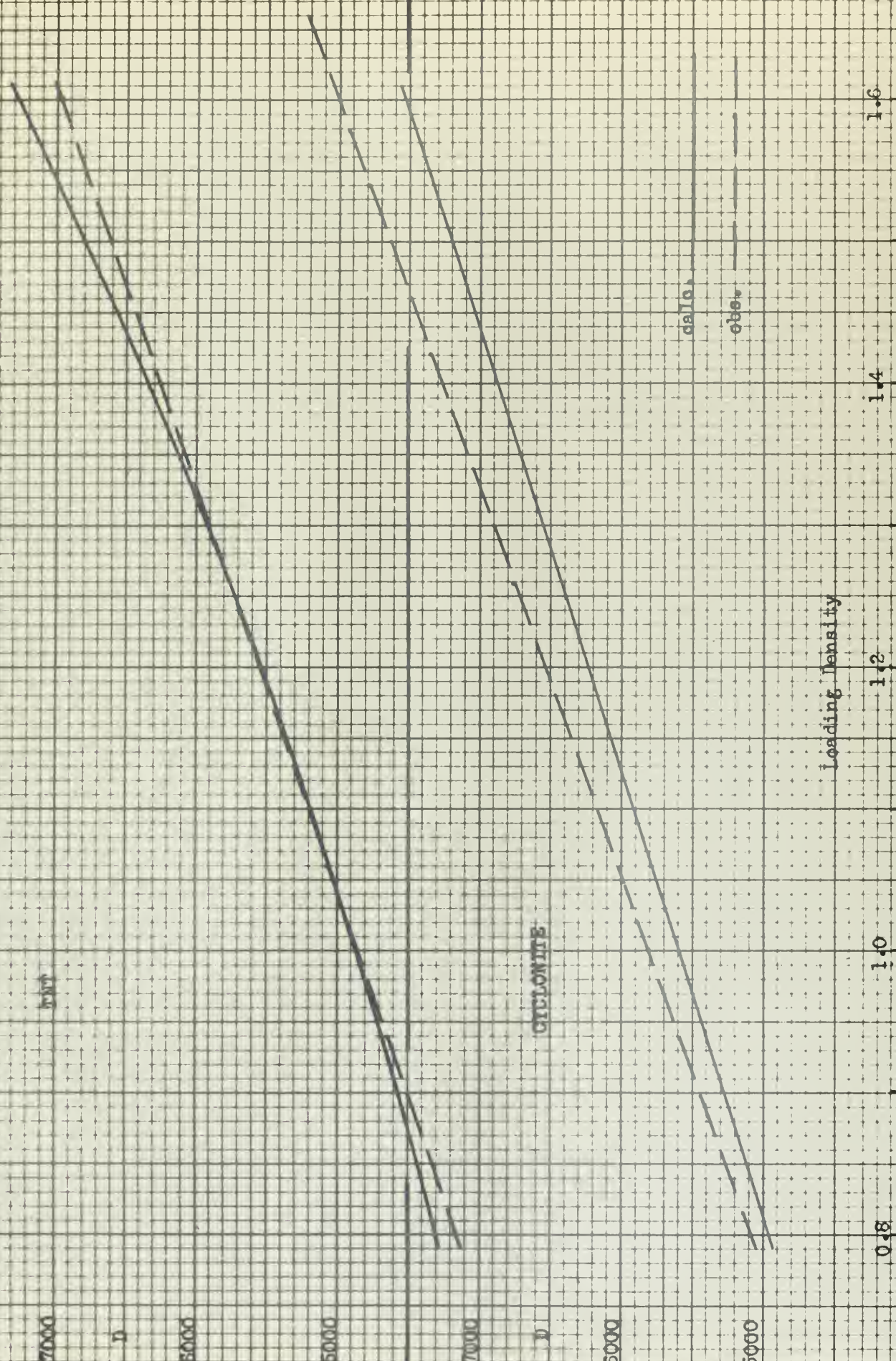
1.4

1.6

calc.

obs.





APPENDIX A

RELATION OF DETONATION VELOCITY TO $c + u$ AT VARIOUS POINTS

ON THE RANKINE-HUGONIOT CURVE

In a previous section, it was shown that at the point B, Figure 3, the detonation velocity was equal to $c + u$ in accordance with the Chapman-Jouguet condition. It is of interest to determine the relation at points other than B. Figure 3 is reproduced below for convenient reference.

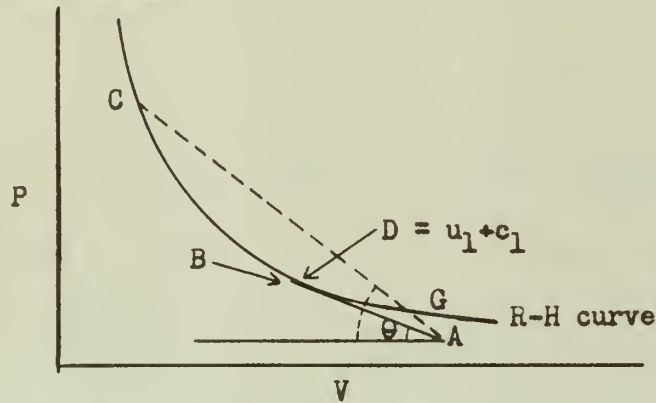


Figure 3

Generalized Rankine-Hugoniot Curve

It is well established that the sonic velocity is related to the slope of an isentropic PV curve by

$$c_1^2 = v_1^2 \left(- \frac{\partial P_1}{\partial v_1} \right)_s$$

From Equations 4 and 5, we have the relation

$$(D - u_1)^2 = v_1^2 \frac{P_1 - P_0}{V_0 - V_1}$$

$P_0 V_0$ being evaluated at the point A and $P_1 V_1$ on the R-H curve. From these two equations, it appears that the difference between c_1^2 and

$(D-u_1)^2$ at various points on the R-H curve is

$$c_1^2 - (D-u_1)^2 = v_1^2 \left[\left(-\frac{\partial P_1}{\partial v_1} \right)_s - \frac{P_1 - P_0}{v_0 - v_1} \right] \quad (1)$$

The slopes of the isentrope and R-H curves at any point (P, V) are related by the equation

$$\left(\frac{\partial P}{\partial V} \right)_R = \left(\frac{\partial P}{\partial V} \right)_s + \left[\left(\frac{\partial P}{\partial S} \right)_V \left(\frac{\partial S}{\partial V} \right)_P \right]_R$$

where the subscript R indicates differentiation along the R-H curve.

Rearranging and introducing the Maxwell relation $\left(\frac{\partial P}{\partial S} \right)_V = - \left(\frac{\partial T}{\partial V} \right)_P$ we have

$$\left(-\frac{\partial P}{\partial V} \right)_s - \left(-\frac{\partial P}{\partial V} \right)_R = - \left[\left(\frac{\partial T}{\partial V} \right)_P \left(\frac{\partial S}{\partial V} \right)_P \right]_R \quad (2)$$

From the energy Equation 6 for points on the R-H curve, we have

$$\left(\frac{\partial E_1}{\partial v_1} \right)_R = \frac{1}{2} (v_0 - v_1) \left(\frac{\partial P_1}{\partial v_1} \right)_R - \frac{1}{2} (P_1 + P_0)$$

Substituting for $\left(\frac{\partial E_1}{\partial v_1} \right)_R$ its equivalent given by the first and second laws of thermodynamics yields

$$\left(\frac{\partial S_1}{\partial v_1} \right)_R = \frac{v_0 - v_1}{2T_1} \left[\frac{P_1 - P_0}{v_0 - v_1} - \left(-\frac{\partial P_1}{\partial v_1} \right)_R \right] \quad (3)$$

The sign of quantity on the left-hand side of this equation depends upon the relative slopes of the line joining the initial and final states and the tangent to the curve at the point representing the final state. Two extremes are shown in the figure below. Note that at point B the two lines coincide.

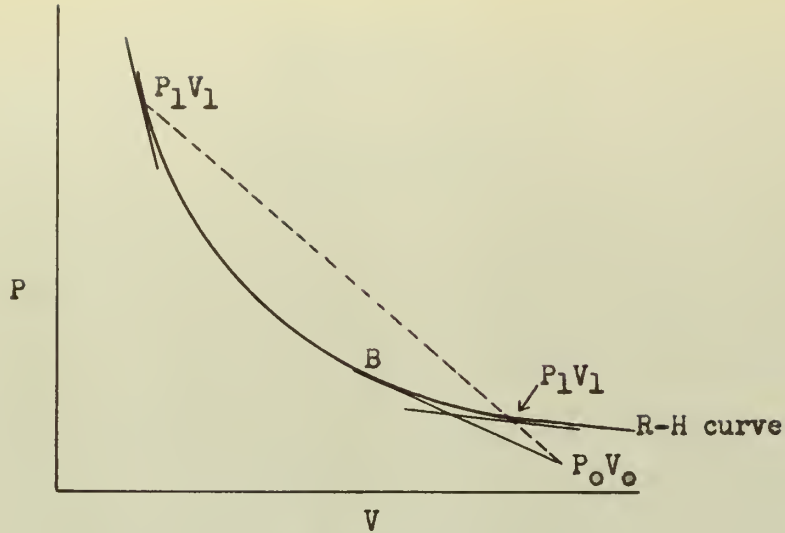


Figure 10

Slope Relations on the R-H Curves.

If the R-H curve is concave upward $\left(\frac{\partial^2 P}{\partial V^2}\right) > 0$, the difference in slopes is negative above B and positive below B. It is certainly reasonable to expect that the R-H curve should have this type curvature for the majority of normal fluids. Solving Equation 3 for the quantity within the square brackets and subtracting from Equation 2, evaluated at the point $(P_1 V_1)$ permits the velocity difference written in Equation 1 to be expressed in terms of variables of known sign. That is

$$c_1^2 - (D-u_1)^2 = - \left(\frac{\partial S_1}{\partial V_1} \right)_R \left[\frac{2T}{V_0 - V_1} + \left(\frac{\partial T_1}{\partial V_1} \right)_P \right] V_1^2 \quad (4)$$

The terms within the square brackets are always positive as is V_1^2 ; therefore the right-hand side is positive for points on the R-H curve above B (where $(\partial S_1 / \partial V_1)_R$ is negative) and negative for points below B, that is where $(\partial S_1 / \partial V_1)_R$ is positive. Hence, as was to be shown, D is less than $c_1 + u_1$ when the final state $(P_1 V_1)$ is above B and is greater than $c_1 + u_1$ when the final state is below B.

APPENDIX B

SECONDARY EFFECTS

The theoretical treatment of the detonation of solid explosives was most conveniently accomplished by neglecting certain effects such as charge diameter and unstable detonation velocities that must be considered in any practical application of the theory. Fundamental investigations of these effects and their ramifications have been made and several theories have been proposed in an effort to explain the observed phenomena. Since a detailed description of the proposed theories sheds little light on the fundamentals of the detonation process, it is believed advisable, for the purpose at hand, to regard them as "second-order" effects and to devote to such effects a very limited treatment.

The effect of charge diameter on the detonation velocity has been observed since the earliest experiments were conducted. This effect is observed as a decrease in the detonation velocity when an explosive is confined in a tube of small diameter. Fortunately, the variation ceases when a certain reasonable diameter is reached, thus the investigation of other parameters can be carried out without the introduction of an additional variable. By the same token, few investigators have undertaken detailed studies of its cause and until recently a generally accepted explanation was not available. A theory proposed by Jones (34) accounts for the observed variation on the basis of lateral losses. During the finite reaction time, the high pressure within the reaction zone is assumed to cause an appreciable lateral expansion with a resultant drop in pressure, temperature and detonation velocity. In other words,

not all of the energy of the explosive is available to maintain the ideal detonation velocity due to lateral dissipation. It can be shown by a detailed mathematical analysis that the effect becomes significant when the radius of the explosive charge is of the same order of magnitude as the reaction zone.

Another phenomenon observed frequently in the detonation of solid explosives is the transition from an unstable detonation velocity (one that is either too high or too low) to the stable value. Whenever an explosive charge is initiated by a priming charge having a different detonation rate, this transition must occur. A theory of the building-up rate as a function of the reaction zone length has been proposed (7) and leads to the conclusion that the ideal velocity is approached asymptotically, half the difference between the initial and final value being covered in a few reaction zone lengths.

If a detonation wave experiences such severe losses that the wave can no longer propagate at the ideal velocity, the phenomenon referred to as "fading" is observed. As in the case of transition from one velocity to another, the length of the reaction zone is a critical feature and theoretical treatments of the phenomenon are based upon the cumulative effects resulting from increased reaction zone lengths.

In summary, it might be observed that if one possessed sufficient information concerning the chemical reaction kinetics to predict the length of the reaction zone under any conditions of pressure, temperature, etc., a more rational approach to many of the technical problems confronting the explosives engineer could be made.

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